



# KINETIC THEORY OF GASES

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# **GASES**

- **Gases are one of the most pervasive aspects of our environment on the Earth. We continually exist with constant exposure to gases of all forms.**
- **The steam formed in the air during a hot shower is a gas.**
- **The Helium used to fill a birthday balloon is a gas.**
- **The oxygen in the air is an essential gas for life.**

# Properties of Gases

## **1) Gases are highly compressible**

An external force compresses the gas sample and decreases its volume, removing the external force allows the gas volume to increase.

## **2) Gases are thermally expandable**

When a gas sample is heated, its volume increases, and when it is cooled its volume decreases.

## **3) Gases have high viscosity**

Gases flow much easier than liquids or solids.

## **4) Most Gases have low densities**

Gas densities are on the order of grams per liter whereas liquids and solids are grams per cubic cm, 1000 times greater.

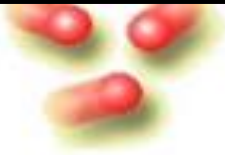
## **5) Gases are infinitely miscible**

Gases mix in any proportion such as in air, a mixture of many gases.

# KINETIC THEORY OF GASES

- To fully understand the world around us requires that we have a good understanding of the behavior of gases. The description of gases and their behavior can be approached from several perspectives.
- The *Gas Laws* are a mathematical interpretation of the behavior of gases.
- However, before understanding the mathematics of gases, a chemist must have an understanding of the conceptual description of gases. That is the purpose of the *Kinetic Molecular Theory*.

# KINETIC THEORY OF GASES



## Remember the assumptions

- Gas consists of large number of particles (atoms or molecules)
- Particles make elastic collisions with each other and with walls of container
- There exist no external forces (density constant)
- Particles, on average, separated by distances large compared to their diameters
- No forces between particles except when they collide

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# Distinction between Ideal gas and Non Ideal gas

Ideal or Perfect gases	Non-ideal or Real gases
1. Ideal gases obey the gas laws at all temperatures and pressures.	1. Non-ideal gases do not obey the gas laws at all temperatures and pressures.
2. Ideal gases obey the ideal gas equation, $PV = nRT$ under all conditions.	2. Non-ideal gases do not obey the ideal gas equation, $PV = nRT$ under all conditions.
3. Here, the volume occupied by gas molecules is negligible in comparison with the total volume of gas.	3. In this case, the volume occupied by gas molecules cannot be neglected in comparison with the total volume of gas.
4. In this case, intermolecular attraction is negligible under all conditions.	4. Here, intermolecular attraction cannot be neglected.

# Deviations of Real gases from Ideal behaviour (From Gas Laws)

- I) Deviations form Boyle's Law:-

$$P \propto \frac{1}{V}$$

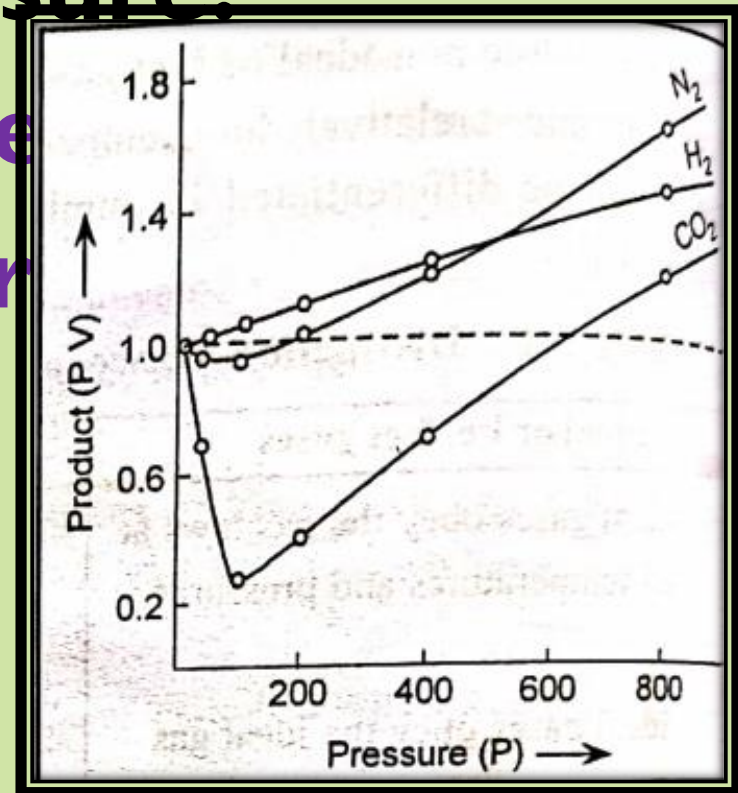
- Compressibility Factor

$$Z = \frac{PV}{nRT}$$

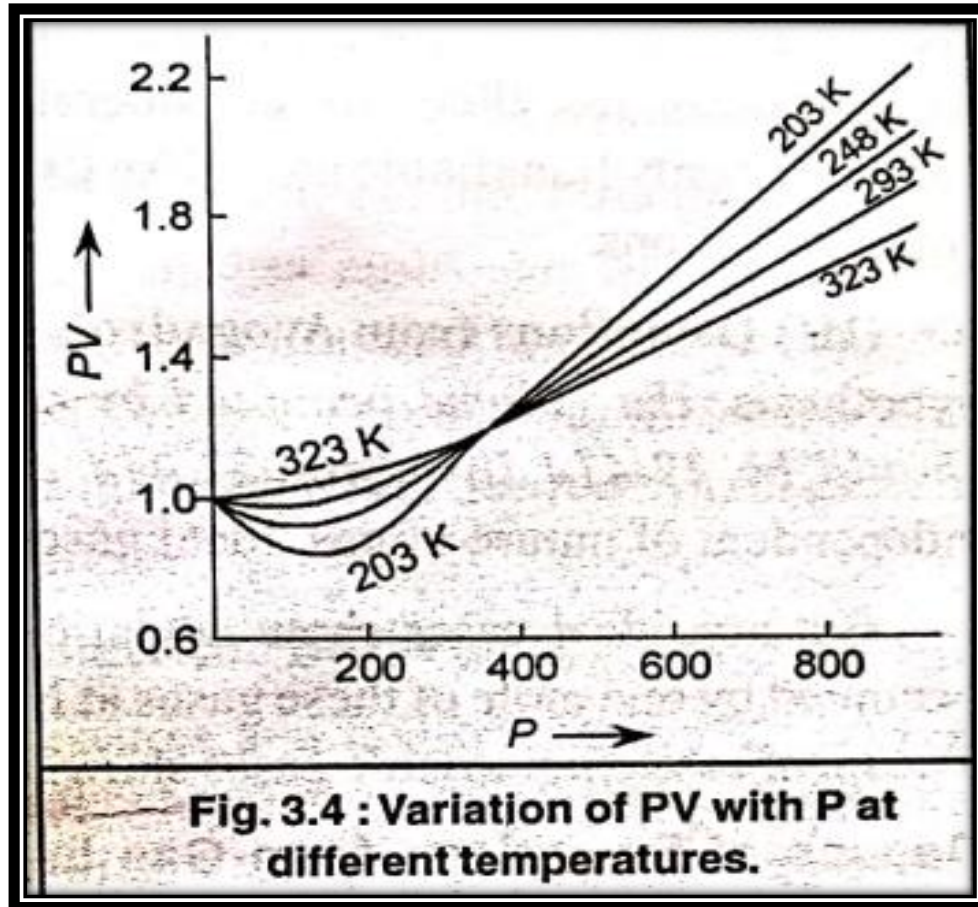


# Deviations of Real gases from Ideal behaviour (From Gas Laws)

- **Effect of Pressure:**
- **A) At Low Pressure**
- **B) AT High Pressure**
- 



# Effect of Temperature:-



# Deviations from Charle's Law

(II) Deviations from Charles's Law: At constant pressure, the volume of a given mass of a gas increases or decreases by  $\frac{1}{273}$  of its volume at  $0^\circ\text{C}$  (or  $273\text{ K}$ ) for every degree rise or fall in temperature. If  $V_t$  is the volume of gas at  $t^\circ\text{C}$  and  $V_0$  is the volume at  $0^\circ\text{C}$ , then Charles's law can be represented mathematically as,

$$V_t = V_0(1 + \alpha t)$$

Where,  $\alpha$  is the coefficient of cubical expansion.

# Deviations from Avogadro's Law

(III) Deviations from Avogadro's law : According to Avogadro's hypothesis, *the volume occupied by one mole of every gas at NTP should be 22.414 litres (or 22.414 dm<sup>3</sup> in S.I.) and it should be independent of nature of gas. Ideal gases obey this value.*

But non-ideal gases show deviations from this value *i.e.* volume occupied by one mole of these gases at NTP is not exactly 22.414 litres. The most easily liquefiable gases show larger deviations.

# Causes of Deviations from Gas Laws

- 1) The actual volume of a gas molecule is negligible in comparison with the total volume of the gas.
- 2) The gas molecules do not exert attractive forces on one another.

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# Van de Waals Equation of state for Real Gases

## Ideal Gas Equation

$$PV=RT$$

- 1) Volume Correction due to size of the molecules:-

$$\text{Corrected (ideal) volume} = V - b$$

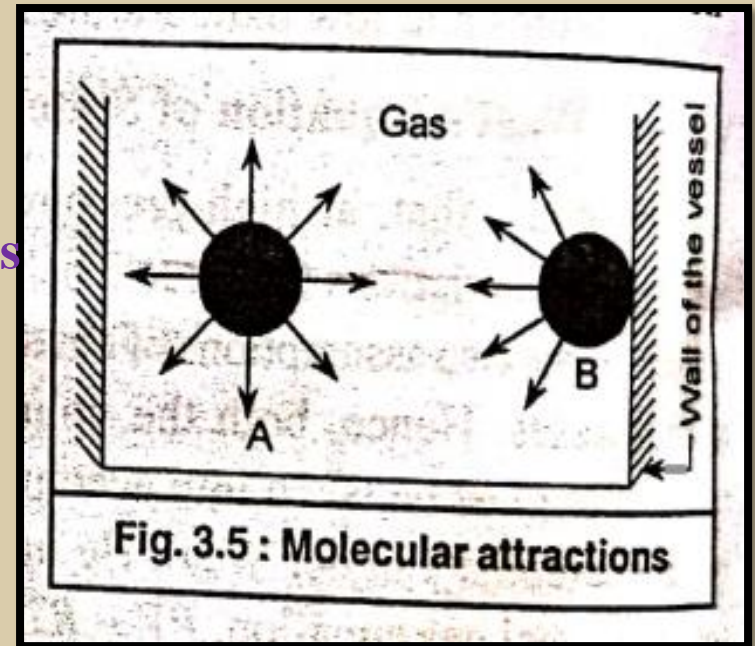
$$\text{Corrected (ideal) volume} = V - nb$$

# Van de Waals Equation of state for Real Gases

- 2) Pressure Correction due to the mutual attraction of the molecules

Corrected (ideal) pressure =  $P + P_a$

$P_a$  = correction term due to attractive forces





# Van de Waals Equation of state for Real Gases

Constants for some gases.

Constants	Gases										
	NH <sub>3</sub>	Ar	CO <sub>2</sub>	CO	Cl <sub>2</sub>	He	H <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub> O
C.G.S. units											
$a$ Atm. lit <sup>2</sup> .mol <sup>-2</sup>	4.17	1.35	3.59	1.49	6.49	0.034	0.024	2.25	1.39	1.36	5.46
$b$ Lit. mole <sup>-1</sup>	0.0371	0.0322	0.0427	0.0399	0.0562	0.0237	0.0266	0.0428	0.0391	0.0318	0.030
S.I. units											
$a$ Nm <sup>4</sup> mol <sup>-2</sup>	0.423	0.137	0.365	0.151	0.659	0.0035	0.0025	0.229	0.141	0.138	0.553
$b$ (m <sup>3</sup> mol <sup>-1</sup> ) x 10 <sup>5</sup>	3.72	3.23	4.28	4.0	5.64	2.38	2.67	4.3	3.92	3.19	3.3

# Van de Waals Equation of state for Real Gases

If the same volume ' $V$ ' is occupied by ' $n$ ' moles of gas, then,

$$d \propto \frac{n}{V} \quad \therefore Pa \propto d^2 \propto \frac{n^2}{V^2} \quad \text{OR} \quad Pa = \frac{an^2}{V^2}$$

$$\text{corrected (ideal) pressure} = P + \frac{an^2}{V^2},$$

$$Pa = \frac{an^2}{V^2} \quad \therefore a = \frac{Pa \cdot V^2}{n^2}$$

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT$$

$$\left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

# Van de Waals Equation of state for Real Gases

$Pa$  = Attractive force on a single molecule  $\times$   
Number of molecules striking the wall

*i.e.*  $Pa \propto d \times d$

or  $Pa \propto d^2$

If  $V$  is the volume occupied by one mole of the gas, then

$$d \propto \frac{1}{V}$$

Hence,  $Pa \propto d^2 \propto \frac{1}{V^2}$

$$\therefore Pa = \frac{a}{V^2}$$

where, ' $a$ ' is proportionality constant and is called *coefficient of attraction*. The term  $\frac{a}{V^2}$  is a measure of attractive force of the molecules

# Explanation of real gases behavior by Van der waal's equation

- 1) At low or intermediate pressure

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$\left(P + \frac{a}{V^2}\right)(V) = RT$$

$$PV + \frac{a}{V} = RT$$

$$\text{or } PV = RT - \frac{a}{V}$$

# Explanation of real gases behavior by Van der waal's equation

- **2) At high pressure**

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$P(V - b) = RT$$

$$PV - Pb = RT$$

$$PV = RT + Pb$$

Alternatively, we can write the van der Waal's equation as,

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

$$\text{i.e. } P(V - b) + a\left(\frac{1}{V} - \frac{b}{V^2}\right) = RT$$

$$P(V - b) = RT$$

$$\text{i.e. } PV - Pb = RT$$

$$\text{or } PV = RT + Pb$$

# Explanation of real gases behavior by Van der waal's equation

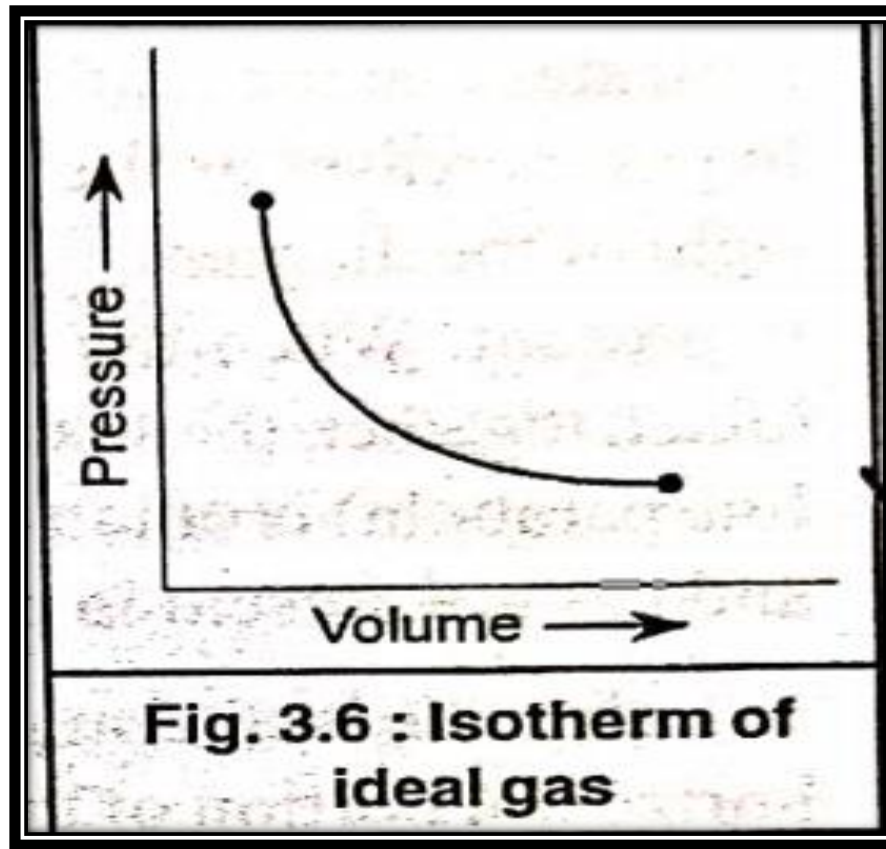
*(iii) At extremely low pressures and extremely high temperatures:*

$$PV = RT$$

*(iv) Exceptional behaviour of hydrogen and helium :*

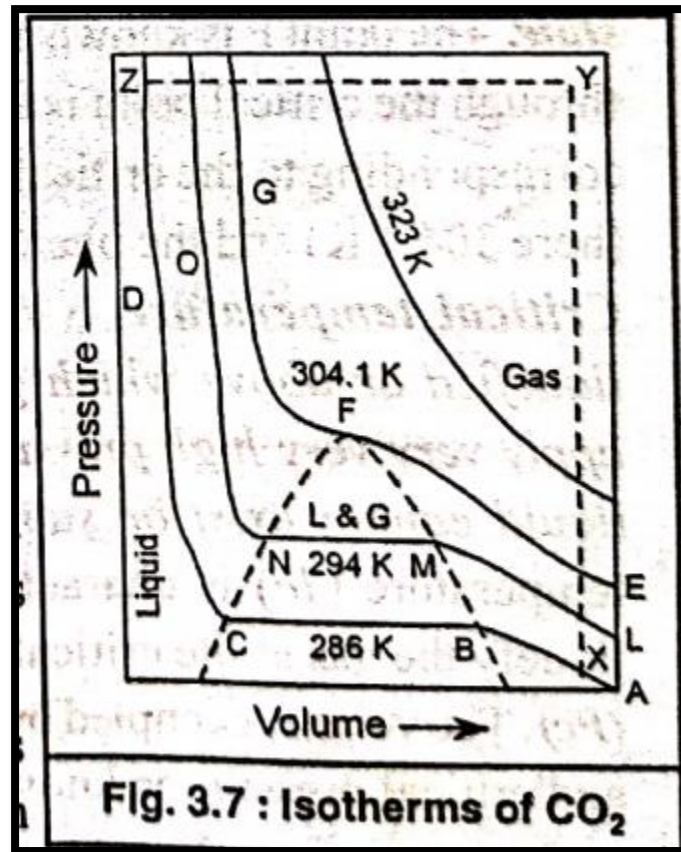
$$P(V - b) = RT \quad \text{or} \quad PV = RT + Pb$$

# Isotherms of gas



# PV – Isotherms of Real Gases (Andrew's isotherms)

## Andrew's Experiment on the P-V-T Relations of Carbon Dioxide and Critical Phenomena.





# Relationship between Critical constants and Van der Waals constant

We have van der Waal's equation for one mole of the gas as,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$\therefore PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

Multiplying by  $V^2$ , we get,

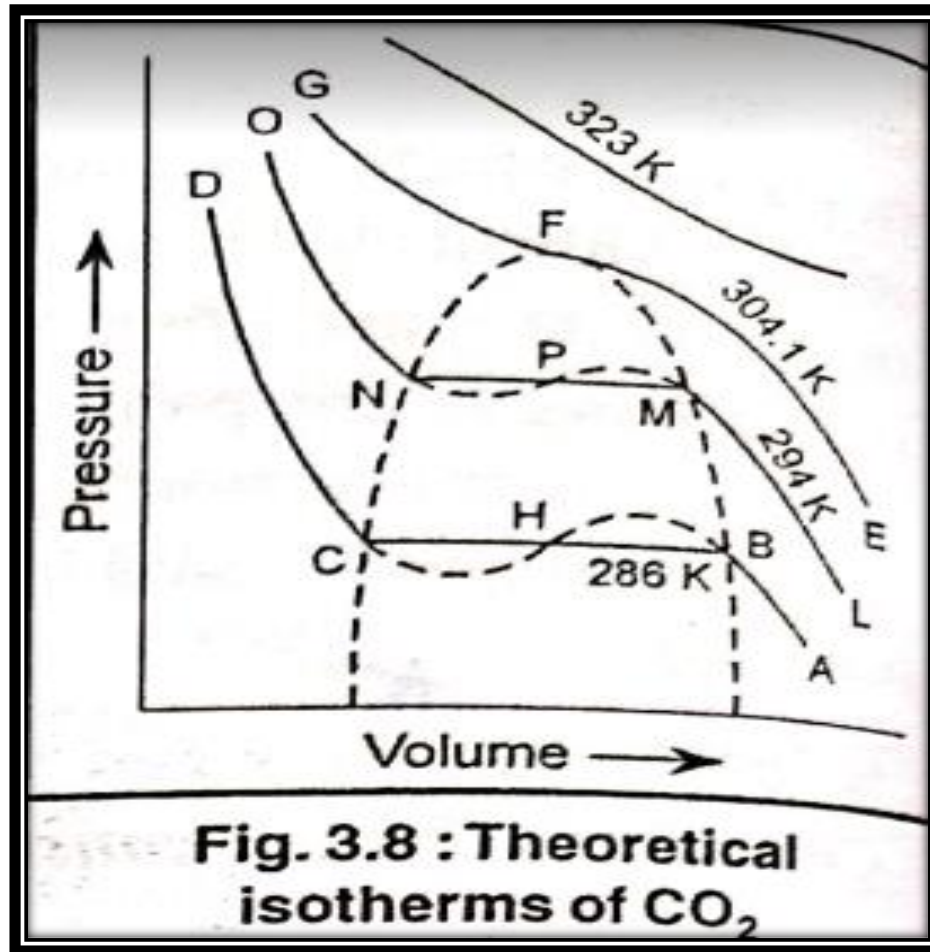
$$PV^3 - PbV^2 + aV - ab = RTV^2$$

$$\therefore PV^3 - PbV^2 - RTV^2 + aV - ab = 0$$

Dividing by  $P$ , we get,

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \left(\frac{a}{P}\right)V - \frac{ab}{P} = 0$$

# Relationship between Critical constants and Van der Waals constant



# Relationship between Critical constants and Van der Waals constant

$$V = V_c$$

or  $V - V_c = 0$

$$\therefore (V - V_c)^3 = 0$$

$$\therefore V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0$$

This equation must be identical with van der Waal's equation (3.3) when  $T = T_c$  and  $P = P_c$ , i.e.

$$V^3 - \left(b + \frac{RT_c}{P_c}\right) \cdot V^2 + \left(\frac{a}{P_c}\right) \cdot V - \frac{ab}{P_c} = 0 \quad \dots\dots\dots (3.5)$$

# Relationship between Critical constants and Van der Waals constant

On comparing and equating the coefficients in equations (3.4) and (3.5), we get,

$$3V_c = b + \frac{RT_c}{P_c} \dots\dots\dots (3.6)$$

$$3V_c^2 = \frac{a}{P_c} \dots\dots\dots (3.7)$$

and  $V_c^3 = \frac{ab}{P_c} \dots\dots\dots (3.8)$

Dividing equation (3.8) by (3.7), we get,

$$\frac{V_c^3}{3V_c^2} = \frac{ab}{P_c} \times \frac{P_c}{a}$$

# Relationship between Critical constants and Van der Waals constant

$$\text{i.e. } \frac{V_c}{3} = b$$

$$\text{Thus, } \boxed{V_c = 3b}$$

Putting this value of  $V_c$  in equation (3.7), we get,

$$3(3b)^2 = \frac{a}{P_c}$$

$$\text{i.e. } 27b^2 = \frac{a}{P_c}$$

$$\boxed{\therefore P_c = \frac{a}{27b^2}}$$

# Relationship between Critical constants and Van der Waals constant

Substituting the values of  $P_c$  and  $V_c$  in equation (3.6), we get,

$$3(3b) = b + \frac{RT_c}{a/27b^2}$$

i.e.  $9b = b + \frac{RT_c 27b^2}{a}$

$$\therefore 8b = \frac{27b^2 RT_c}{a}$$

$$T_c = \frac{8a}{27Rb}$$

# Relationship between Critical constants and Van der Waals constant

**Values of a and b in terms of critical constants**

$$V_c = 3b$$

$$\therefore \boxed{b = \frac{V_c}{3}}$$

**Putting in eq. 3.10 we get,**

$$P_c = \frac{a}{27 \times (V_c/3)^2} = \frac{a}{27 \times (V_c^2/9)} = \frac{a}{3V_c^2} ;$$

$$\therefore \boxed{a = 3V_c^2 \cdot P_c}$$

# Relationship between Critical constants and Van der Waals constant

the values of  $a$  and  $b$  are generally calculated from  $T_c$  and  $P_c$  not accurate.

We have, 
$$T_c = \frac{8a}{27Rb} \quad \text{and} \quad P_c = \frac{a}{27b^2}$$

Taking the ratio,  $T_c / P_c$  we get,

$$\frac{T_c}{P_c} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R}$$

$$\boxed{b = \frac{RT_c}{8P_c}}$$



## Relationship between Critical constants and Van der Waals constant

Now, taking the ratio,  $T_c^2 / P_c$ , we get,

$$\frac{T_c^2}{P_c} = \frac{64 a^2}{27 \times 27 \times R^2 \cdot b^2} \times \frac{27 b^2}{a} = \frac{64 a}{27 R^2}$$

$$\therefore a = \frac{27 R^2 \cdot T_c^2}{64 P_c}$$

# Relationship between Critical constants and Van der Waals constant

- The value of R in terms of critical constants

$$\text{We know that, } 3V_c = b + \frac{RT_c}{P_c}$$

$$\text{But, } b = \frac{V_c}{3}$$

$$\therefore 3V_c = \frac{V_c}{3} + \frac{RT_c}{P_c}$$

$$\therefore 3V_c - \frac{V_c}{3} = \frac{RT_c}{P_c}$$

$$\therefore \frac{8V_c}{3} = \frac{RT_c}{P_c}$$

$$\therefore R = \frac{8P_c \cdot V_c}{3T_c}$$

$$\therefore R = \frac{2.67 P_c \cdot V_c}{T_c}$$

# Limitations of Van der Waals equation

(i) Experimental evidence shows that at a temperature near the critical temperature and at very high pressures, the real gases show deviations from van der Waal's equation also.

(ii) At high pressures and low temperatures, van der Waal's curves deviate from the observed curves.

(iii) Phenomenon of solidification cannot be explained by this equation.

(iv) From the van der Waal's equation we have,  $\frac{RT_c}{P_c V_c} = 2.67$ .

But in majority of the cases, the experimental value of  $\frac{RT_c}{P_c V_c}$  is 3.7.

# Problems

① Calculate the weight of propane ( $C_3H_8$ ) in a  $5 \times 10^{-3} \text{ m}^3$  cylinder at 398 K and  $1.01 \times 10^7 \text{ Nm}^{-2}$  pressure, using the ideal gas equation. ( $R = 8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$ .)

**Solution : Formula :  $PV = nRT$**

**Given :**  $P = 1.01 \times 10^7 \text{ Nm}^{-2}$ ,  $V = 5 \times 10^{-3} \text{ m}^3$ ,  $R = 8.314 \text{ J}$ ,  
 $T = 398 \text{ K}$ ,  $n = ?$

$$\text{Thus, } n = \frac{PV}{RT} = \frac{1.01 \times 10^7 \times 5 \times 10^{-3}}{8.314 \times 398}$$
$$= 15.26$$

$$\text{Now, No. of moles, } n = \frac{\text{Wt.}}{\text{Mol. Wt.}}$$

$$\therefore \text{Wt.} = n \times \text{Mol. Wt. of propane in kg}$$

$$= 15.26 \times 44 \times 10^{-3} \text{ (kg)}$$

$$= 0.6714 \text{ kg.}$$

2 Calculate the pressure at which one mole of ammonia occupies  $1 \times 10^{-3} \text{ m}^3$  volume at 300 K using, (i) ideal gas equation and (ii) van der Waal's equation.

$$[a = 0.422 \text{ Nm}^4 \text{ mol}^{-2}, b = 3.7 \times 10^{-5} \text{ m}^3, R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}.]$$

**Solution :** We have (i)  $PV = RT$ , for one mole of a gas,

$$\therefore P = \frac{RT}{V} = \frac{8.314 \times 300}{1 \times 10^{-3}} = 2.494 \times 10^6 \text{ Nm}^{-2} \text{ (or Pascal)}$$

(ii) We have van der Waal's equation for one mole of a gas as,

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT$$

$$\text{Thus, } \left( P + \frac{0.422}{(10^{-3})^2} \right) (1 \times 10^{-3} - 3.7 \times 10^{-5}) = 8.314 \times 300$$

$$\text{i.e.} \quad \left( P + \frac{0.422}{10^{-6}} \right) (0.000963) = 2494.2$$

$$\text{i.e.} \quad (P + 4.22 \times 10^5) (9.63 \times 10^{-4}) = 2.4942 \times 10^3$$

$$\text{i.e.} \quad 9.63 \times 10^{-4} P + 406.386 = 2.4942 \times 10^3$$

$$9.63 \times 10^{-4} P = 2494.2 - 406.386 = 2087.814$$

$$\therefore P = \frac{2087.814}{9.63 \times 10^{-4}} = 216.8 \times 10^4 = 2.168 \times 10^6 \text{ Nm}^{-2} \text{ or Pascal.}$$

4 Acetone has the van der Waal's constants as,  $a = 1.406 \text{ Nm}^4 \text{ mol}^{-2}$ ,  $b = 9.94 \times 10^{-5} \text{ m}^3$  and  $R = 8.31 \text{ JK}^{-1} \text{ mol}^{-1}$ . Find the critical volume, critical temperature and critical pressure of acetone.

**Solution :** We have

$$(i) V_c = 3b = 3 \times 9.94 \times 10^{-5} = 2.982 \times 10^{-4} \text{ m}^3.$$

$$(ii) T_c = \frac{8a}{27Rb} = \frac{8 \times 1.406}{27 \times 8.31 \times 9.94 \times 10^{-5}} = 504.3 \text{ K}$$

$$(iii) P_c = \frac{a}{27b^2} = \frac{1.406}{27(9.94 \times 10^{-5})^2} = 5.27 \times 10^6 \text{ Nm}^{-2}$$

or Pascal

7 Calculate van der Waal's constants for ethane. It's critical temperature and critical pressure are 282 K and  $51.41 \times 10^5 \text{ Nm}^{-2}$  respectively. ( $R = 8.31 \text{ JK}^{-1} \cdot \text{M}^{-1}$ )

$$(i) a = \frac{27R^2 \cdot T_c^2}{64 P_c} = \frac{27 \times (8.31)^2 (282)^2}{64 \times 51.41 \times 10^5} = 0.4506 \text{ Nm}^4 \cdot \text{mol}^{-2}.$$

$$(ii) b = \frac{RT_c}{8 P_c} = \frac{8.31 \times 282}{8 \times 51.41 \times 10^5} = 5.698 \times 10^{-5} \text{ m}^3$$